UNCLASSIFIED

AD NUMBER AD850966 **NEW LIMITATION CHANGE** TO Approved for public release, distribution unlimited **FROM** Distribution authorized to U.S. Gov't. agencies and their contractors; Administrative/Operational Use; MAR 1969. Other requests shall be referred to Air Force weapons Laboratory, Attn: WLDC, Kirtland AFB, NM.87117-6008. **AUTHORITY** AFWL ltr, 30 Nov 1971

RAPID INSTRUMENTATION METHODS FOR WATER POLLUTION ANALYSIS

Michael G. MacNaughton

Capt

USAF

TECHNICAL REPORT NO. AFWL-TR-69-22

March 1969

D D C D C APR 2 8 1969

AIR FORCE WEAPONS LABORATORY

Air Force Systems Command Kirtland Air Force Base New Mexico

This document is subject to special export controls and each transmittal to foreign governments or foreign nationals may be made only with prior approval of AFWL (WLDC) , Kirtland AFB, NM, 87117

ति क्षेत्रक्ति क्ष	-
CECTI	WHITE SECTION [
203	EUFF SECTION D
JULES PROFESTS	미
1-SHEPC-TION	
	AVAILABILITY CODES ALL and of SPECIAL

AIR FORCE WEAPONS LABORATORY Air Force Systems Command Kirtland Air Force Base New Mexico

When U. S. Government drawings, specifications, or other data are used for any purpose other than a definitely related Government procurement operation, the Government thereby incurs no responsibility nor any obligation whatsoever, and the fact that the Government may have formulated, furnished, or in any way supplied the said drawings, specifications, or other data, is not to be regarded by implication or otherwise, as in any manner licensing the holder or any other person or corporation, or conveying any rights or permission to manufacture, use, or sell any patented invention that may in any way be related thereto.

This report is made available for study with the understanding that proprietary interests in and relating thereto will not be impaired. In case of apparent conflict or any other questions between the Government's rights and those of others, notify the Judge Advocate, Air Force Systems Command, Andrews Air Force Base, Washington, D. C. 20331.

DO NOT RETURN THIS COPY. RETAIN OR DESTROY.

RAPID INSTRUMENTATION METHODS FOR WATER POLLUTION ANALYSIS

Michael G. MacNaughton Captain USAF

TECHNICAL REPORT NO. AFWL-TR-69-22

This document is subject to special export controls and each transmittal to foreign governments or foreign nationals may be made only with prior approval of AFWL (WLDC), Kirtland AFB, NMex 87117. Distribution is limited because of the technology discussed in the report.

FOREWORD

This research was performed under Program Element 62301F, Project 5713, Task 25.

Inclusive dates of research were 1 December 1968 to 1 February 1969. The report was submitted 20 February 1969 by the Air Force Weapons Laboratory Project Officer, Captain Michael G. MacNaughton (WLDC).

Information in this report is embargoed under the U.S. Export Control Act of 1949, administered by the Department of Commerce. This report may be released by departments or agencies of the U.S. Government to departments or agencies of foreign governments with which the United States has defense treaty commitments, subject to approval of AFWL (WLDC).

The author wishes to express appreciation to Major Donald G. Silva for his help in preparing this report.

This report has been reviewed and is approved.

Michael G. MacNAUGHTON
Captain, USAF

Captain, USAF Project Officer

CLIPM M. WHITEHEAD

Chief, Civil Engineering Branch

GEORGE C. DARBY, JR.

Colonel, USAF

Chief, Development Division

ABSTRACT

(Distribution Limitation Statement No. 2)

Three new methods are described for determining the pollution loading on a waste treatment plant or a stream. These are Total Organic Carbon (TOC), Total Oxygen Demand (TOD), and the Carbon Dioxide Demand (CO₂D). All of these can be used to replace or supplement the conventional Biochemical Oxygen Demand (BOD) and Chemical Oxygen Demand (COD) procedures. The use of these newer methods will provide more reproducible results and will reduce the analysis time from hours (COD) and days (BOD) to an almost instantaneous readout. Graphs which show the relationship between the three techniques and the conventional COD and BOD tests are included for industrial and domestic wastes.

This page intentionally left blank.

CONTENTS

Section		Page
I	BACKGROUND AND INTRODUCTION	1
II	TOTAL ORGANIC CARBON	3
III	TOTAL OXYGEN DEMAND	8
IV	CARBON DIOXIDE DEMAND TEST	12
v	CORRELATION BETWEEN BOD, COD, AND RAPID INSTRUMENTAL	
	METHODS	15
VI	CONCLUSIONS	22
	Distribution	25

V

ILLUSTRATIONS

Figure		Page
1	Diagram of a Total Carbon Analyzer	5
2	Calibration Curve for Total Organic Carbon Analysis (Acetic Acid Standards)	6
3	Diagram of the Total Oxygen Demand Analyzer (Ref. 6)	9
4	Diagram of the Carbon Dioxide Demand Analyzer (Ref.8)	13
5	COD, TOC, CO ₂ D Relationships for an Ethvl Cellulose Industrial Waste (Ref. 8)	17
6	COD/TOD Relationship for a Phenolic Industrial Waste (Ref. 6)	18
7	BOD, COD, and TOD Relationships for the Effluent of a Primary Sewage Treatment Plant (Ref. 6)	18
8	BOD, COD, and TOC Relationships for the Effluent of a Primary Sewage Treatment Plant (Ref. 8)	19
9	COD, CO ₂ D, and TOC Relationships for the Effluent of a Primary Sewage Treatment Plant (Ref. 8)	20
10	COD, CO ₂ D, and TOC Relationships for the Effluent of a Secondary Sewage Treatment Plant (Ref. 8)	20
11	BOD, COD, CO2D, and TOC Relationships for the Effluent of a Secondary Sevage Treatment Plant (Ref. 8)	21

TABLES

Table		Page
I	Analysis of Standard Solutions for Carbon (Ref. 5)	4
II	Interference with Inorganic Carbon Determinations (Ref. 7)	7
III	Comparison of COD and TOD (Ref. 6)	10
IV	ANION Interferences with TOD Analysis	10
V	Interference of D.O. in TOD Analysis	11
VI	Analysis of _andard Solutions for CO2D (Ref. 8)	13
VII	Interferences with CO ₂ D Analysis (Ref. 8)	14
VIII	Comparison of COD and Carbon (Ref. 9)	16

This page intentionally left blank.

SECTION I

BACKGROUND AND INTRODUCTION

As the field of environmental engineering expands and becomes larger and increasingly more technical, it is harder for the practicing civil and bio-environmental engineer to be cognizant of the literature and new advances in technology.

In conducting a research and development program in environmental engineering, the Air Force Weapons Laboratory must keep abreast of the latest technology in the field. Frequently, occasions arise where summaries of information can easily be put together and distributed to the practicing engineer to acquaint him with the latest available technology. This report is the first of a series of compilations of new technology and is intended for the field civil and bioenvironmental engineer.

One of the results of organic pollution is the reduction of dissolved oxygen in a stream, river, or lake. This lack of dissolved oxygen, caused by bacterial degradation of organics, evidences itself by the much publicized fish kills, odors, murky waters, etc. Since this loss of oxygen is caused primarily by biological activity, the test that has been the standard for over 40 years has been the biochemical oxygen demand test (BOD). This test measures the oxygen consumed by a waste sample in 5 days at 20° C (Ref. 1). Unfortunately, this test takes 5 days to complete and presents a time delay problem for effective treatment plant operation, or pollution evaluation. The precision of the BOD test leaves much to be desired. A \pm 20% standard deviation has been reported for tests run by 34 water analysis laboratories on a test solution of 1.5 mg glucose and 1.5 mg glutamic acid (Ref. 2). Numerous inaccuracies are inherent in the analysis: biological seed variability, toxic chemical effects, dilution, and the possible need to acclimate the seed.

To supplement and possibly replace the BOD test with improved reproducibility and a shorter analysis time, the chemical oxygen demand (COD) test has been used in many cases. This procedure involves digestion with potassium dichromate and concentrated sulfuric acid, and back titration of the excess oxidant with ferrous ammonium sulfate. The COD is also a laborious test which takes 2 hours, but results in increased reproducibility of \pm 8% (Ref. 2).

Because of the time involved with the BOD and COD tests, considerable emphasis has been given to development of quick, reproducible methods which would still be relatable to the BOD test. The report describes three of these new methods: Total Organic Carbon (TOC),* (CO₂D),* and Total Oxygen Demand (TOD).*

^{*} Patented by Dow Chemical

SECTION 11

TOTAL ORGANIC CARBON

For any oxidation reaction, the relation between oxygen and the material oxidized is fixed and can be determined from the reaction equation. For example, a simplification of the biological oxidation of glucose is shown in equation 1. The "theoretical oxygen demand" is 1.07 gm of oxygen per gm of glucose (Ref. 3).

$$c_6 H_{12} O_6 + 6 O_2 \longrightarrow 6 C O_2 + 6 H_2 O$$
 (1)

The basic objective of pollution measurement methods is to determine the amount of the biologically degradable organics or carbon which will be converted to CO_2 and water, using the available oxygen. Until recently the measurement of carbon in low concentrations has been lengthy and difficult. Numerous wet oxidation systems have been used in which strong oxidizing agents convert the organics to CO_2 , which is then measured manometrically, titrimetrically, or gravimetrically (Ref. 4). The TOC technique developed by the Analytical Service at Dow Chemical makes this determination effortless. Table I shows an analysis of standard solutions for carbon.

Basically, the TOC analyzer consists of three sections: oxidizing system, infrared analyzer, and stripchart recorder. Figure 1 shows a schematic of a TOC analyzer built at the Air Force Weapons Laboratory. The analysis involves the injection of a sample into the combustion tube with the CO₂ produced from the combustion measured by the nondispersive infrared analyzer. The output is recorded on the stripchart.

The total carbon combustion tube is constructed of vycor or fused silica glass, has platinum gauze to act as a catalyst, and is kept at 950°C in a tube furnace. The inorganic carbon combustion tube consists of the same type of glass but has glass beads coated with phosphoric acid and is held at 150°C. By the difference between the total carbon and the inorganic carbon, the organic portion can be calculated. Since the recorded peaks on the strip chart are not absolute values of carbon, a standard curve must be made before quantitative analyses can be performed. A series of standards is prepared containing 0 to 160 mg/liter of

Table I

ANALYSIS OF STANDARD SOLUTIONS FOR CARBON (Ref. 5)

		Carbon	
Compound	Calcd (mg/lit)	Found (mg/lit)	Recovered (%)
Benzoic acid	68.8	68.2	99.1
Pheno1	76.6	76.9	100.4
Sucrose	104.8	104.5	99.7
Glycine	100.7	100.3	99.6
Pyridine	105.6	104.2	98.7
Urea	100.0	99.8	99.8
Sodium cyanide	122.5	120.5	98.4
Acetanilide	75.4	75.4	100.0
p-Nitroaniline	106.2	105.4	99.2
4-Aminoantipyrine	111.5	110.2	98.8
Sulfanilic acid	89.3	89.3	100.0
Diphenylaminesulfonate, Ba salt	87.8	87.4	99.5
di-Methionine	103.0	102.5	99.5
2,4,6-Trichlorophenol	75.4	75.0	99.5
Sodium carbonate	99.5	99.4	99.9
Acetic acid in 20° NaCl	100.0	100.0	100.0
Acetic acid in 20% CaCl ₂	100.0	99.1	99.1
•			

٨

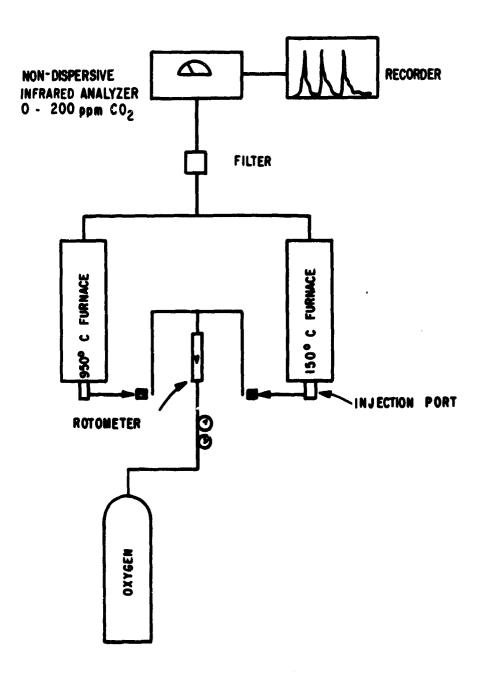


Figure 1. Diagram of a Total Carbon Analyzer.

carbon. These are made by adding 0, 10, 20, 30, and 40 ml of standard i gm/liter acetic acid (1 mg acetic acid per ml and .4 mg carbon per ml), and distilled water up to 100 ml. An acetic acid-carbonate combination may be used in place of acetic acid since it is more stable with respect to $\rm CO_2$ loss or gain. Using these standards, a curve such as that shown in Figure 2 is developed. The size of the injected sample should be approximately 20 μ l and the gas flow rate will vary depending upon the IR detector but is in the range of 50-200 ml/min. The gas can be either oxygen, as was reported in the original work (Ref. 5), or any inert, carbon-dioxide-free gas such as helium or nitrogen. It is not fully understood why the $\rm CO_2$ is produced with the inert gases.

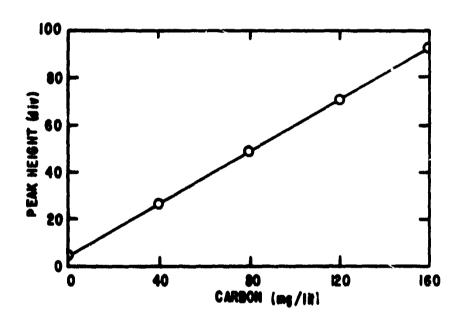


Figure 2. Calibration Curve for Total Organic Carbon Analysis (Acetic Acid Standards)

Some compounds were found to interfere with the determination of the inorganic carbon portion of a waste. Table II gives a summary of their substances and the temperature at which they form CO₂ or undergo acid hydrolysis. Only tartronic acid was found to interfere at the temperature of 150°C recommended. Larger concentrations of nitric or nitrous acids than those used will give interference at 150°C (Ref. 7).

Table II

INTERFERENCE WITH INORGANIC CARBON DETERMINATIONS (Ref. 7)

Compound	Concn.	Temperature			
	(gm/lit)	150°C	175°C	200°C	
Urea	0.5000	None	Slight	Definite	
Oxalic acid	1.0506	None	Definite	Definite	
DL-Malic acid	1.1174	None	Slight	Definite	
Malonic acid	1.10406	None	Slight	Definite	
Citric acid	1.6010	None	Definite	Definite	
Tartronic acid	1.0000	Definite	Definite	Definite	
Sucrose	2.8525	None	Definite	Definite	

NOTE: Substances showing no interference at temperatures tested: calcium acetate, formic acid, methanol, butyric acid, o-phthalic acid, benzoid acid, chloroform, acetic acid, picric acid, sodium bisulfite, sodium chloride.

SECTION III

TOTAL OXYGEN DEMAND

The total oxygen demand method measures the amount of oxygen required to oxidize the substances in an aqueous sample. Figure 3 is a flow diagram of the system which is being marketed by Ionics Inc., under a license from Dow Chemical (Ref. 6). The aqueous sample is introduced into the combustion furnace with a nitrogen carrier gas containing a low oxygen content, normally 200 ppm. The impurities are oxidized by depleting the oxygen on a platinum catalyst at a temperature of 900°C, and this oxygen is replenished from the carrier gas, causing a momentary depletion of the 0, in the gas stream. A silver-lead fuel cell acts as the detector which produces a current output proportional to the oxygen content of the effluent gas stream. Since the oxygen concentration decreases, what is seen on a potentiometric recorder is actually a negative peak. The sample can either be injected as in the TOC analyzer or aspirated automatically such as in the commercial TOD equipment (Ref. 6). The oxygen in the carrier gas is obtained from a standard nitrogen-oxygen mixture or by an oxygen-permeable tube in the nitrogen supply line. Unlike the carbon analysis, hydrogen, combined nitrogen, and sulfur as well as carbon are measured. The TOD approaches the theoretical oxygen demand as closely as any method now used. Table III shows a comparison of theoretical and actual oxygen consumption values (Ref. 6).

As seen in Table IV none of the common anions found in waste water interfere in the TOD tests. However, since the TOD measures the oxygen demand in excess of the dissolved oxygen, the results will be affected by dissolved oxygen. Table V shows the TOD of samples with zero dissolved oxygen and samples saturated with dissolved oxygen.

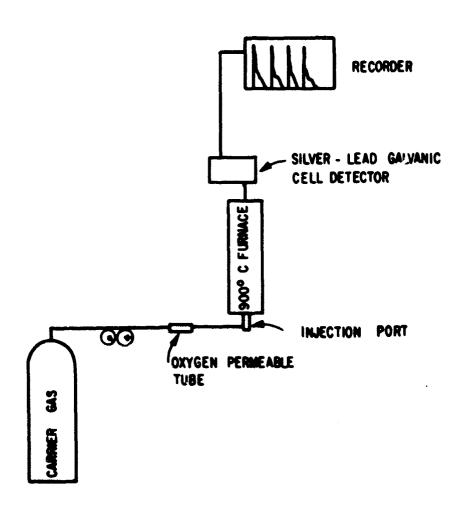


Figure 3. Diagram of the Total Oxygen Demand Analyzer (Ref. 6)

Table III

COMPARISON OF COD AND TOD (Ref. 6)

Compound	Conc.	COD (mg/lit)		Conc. COD (mg/lit) TOD (mg/	TOD (mg/	lit)
	(gm/lit)	Calc.	Found	Calc.	Found	
p-Nitroaniline	0.1020	165	163	177	181	
Pyridine	0.0521	111	3	142	134	
Urea	0.2478	0	63	330	339	
Glycine	0.2000	128	129	234	231	
Sodium Cyanide	0.2933	239	86	325	313	
Sucrose	0.1267	142	138	142	132	

Table IV

ANION INTERFERENCES WITH TOD ANALYSIS (Ref. 6)

ANION	TOD		
(1000 mg/lit)	Calc (mg/lit)	Found (mg/lit)	
C1	200	198.2	
HCO3	200	204.5	
so.	200	191.4	
нѕо_	200	196.8	
нро <mark>"</mark>	200	195.2	

Table V

INTERFERENCE OF D.O. IN TOD ANALYSIS (Ref. 6)

Compound	Conc. (mg/lit)	D.O. (mg/lit)	TOD (mg/lit)
Potassium Hydrogen Pthalate (KHP)	170	0	200
кнь	170	8.2	191
KHP	85.1	0	100
КНР	85.1	8.2	91

SECTION IV

CARBON DIOXIDE DEMAND TEST

The CO₂D method of analysis is unique in that it uses CO₂ instead of oxygen to combust the organics. The amount of CO produced is equal to the amount of oxygen used in the oxidation as in the following equations (Ref. 9):

$$C_a H_b N_c O_d + m CO_2 \longrightarrow (m + a) CO + b/2 H_2 O = c/2 N$$
 (2)

$$C_a H_b N_c O_d + n/2 O_2 \longrightarrow a CO_2 + b/2 H O + c/2 N_2$$
 (3)

To balance the oxygen in both equations

$$d + 2m = (m + a) + b/2$$
 (4)

$$d + n = 2a + b/_2$$
 (5)

Subtracting yields

Oxygen in the carrier gas must be removed because it causes an interference since it is a stronger oxidant than CO_2 . This is done by passing the gas through a heated carbon bed which generates a small amount of CO_2 . The quantitative analysis is related to the standard curves the same as in the TOC analysis. Figure 4 is a schematic of the $\mathrm{CO}_2\mathrm{D}$ apparatus and Table VI shows the calculated oxygen demand compared with the experimental oxygen demand determined by the $\mathrm{CO}_2\mathrm{D}$ test (Ref. 8).

Chloride is the main positive interfering substance, and if the oxygen demand is low, it may be necessary to run a blank with the known amount of chloride present in the sample. The reason for the high value may be a secondary reaction of hydrochloric acid with the CO₂ and platinum (Ref. 8).

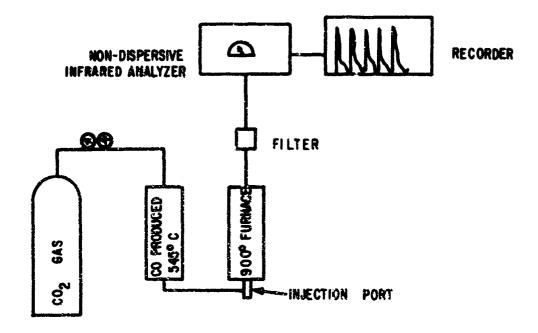


Figure 4. Diagram of the Carbon Dioxide Demand Analyzer (Ref. 8)

Com. v. A		co ₂ D	
Compound	Calcd (mg/lit)	Found (mg/lit)	Recovered (%)
Acetic acid	246	239	97.2
Benzoic acid	250	248	99.2
Oxalic acid	250	244	97.6
Glycine	250	248	99.2
Urea	250	250	100.0
p-Nitroaniline	250	244	97.6
Phenol	245	216	88.2
Sucrose	248	215	86.7
Acetone	173	145	83.8
Ethanol	235	200	85.1
Methanol	238	205	86.1
Ammonium hydroxide	250	204	80.6
Ammonium chloride	150	274	109.6

$$2NH_4C1 + 3CO_2 \longrightarrow N_3 + 3CO + HC1 + H_3O$$
 (6)

$$2HC1 + CO_2 + Pt \longrightarrow CO + H_2O + PtC1_2$$
 (7)

PtCl₂ is probably a very transient material.

Several other inorganic salts interfere negatively. Table VII contains the analysis of several of these solutions, each containing 250 mg/l of oxygen demand and 500 mg/l of the salt. All of these salts yield available oxygen (Ref. 8).

Table VII

INTERFERENCES WITH CO₂D ANALYSIS (Ref. 8)

Compound	Peak Height	% Error
Acetic acid	65.8	
Acetic acid + Na ₂ SC ₄	57.3	-12.9
Acetic acid + NaNO ₂	12.4	-81.2
Acetic acid + NaH ₂ PO ₄ H ₂ O	63.5	- 3.5

SECTION V

CORRELATION BETWEEN BOD, COD, AND RAPID INSTRUMENTAL METHODS

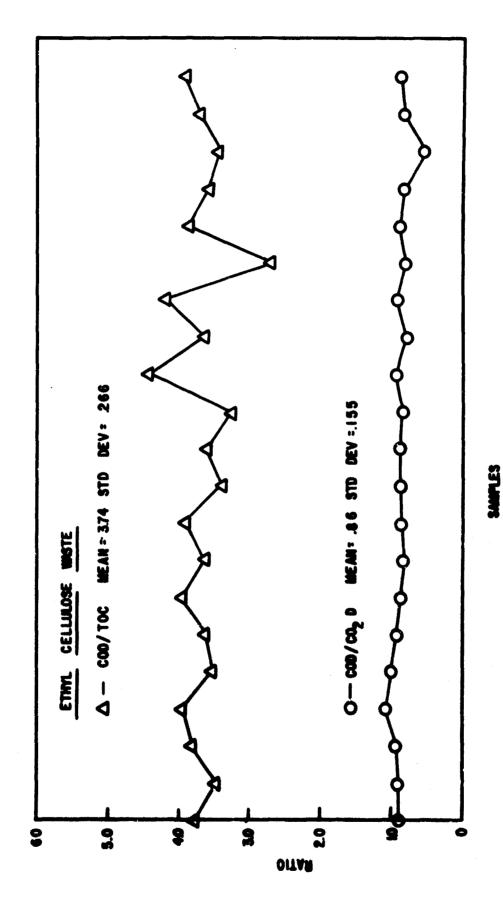
There are many reasons why BOD, COD, TOC, CO₂D, and TOD correlations should be qualified. There are inorganic substances which consume oxygen in aqueous solutions, while there are some organic compounds which create little or no biochemical or chemical oxygen demand. Ferrous iron, sulfites, and sulfides are some compounds that have no carbon but still exert an oxygen demand; pyridine is an example of an organic that will not have a COD. It can be seen from the carbon/COD ratios in Table VIII that in many cases the experimental ratios are close to the theoretical but that there are some ratios that are very different. It is because of these discrepancies that one must know what is in the solution to be analyzed or must have run enough tests to be able to predict the ratio statistically.

Figures 5 and 6 show the $\mathrm{CO}_2\mathrm{D}$, COD , and TOC relationships for various industrial wastes (Refs. 6 and 10). Although a poor correlation sometimes exists between the methods for industrial wastes, domestic wastes which are normally more uniform in their relative consistency show a better correlation. Figures 7 through 11 show the relationship of COD , 5-day BOD, total organic carbon, and $\mathrm{CO}_2\mathrm{D}$ for a municipal waste before and after primary and secondary treatment. As can be seen by Figures 5 through 11, the different instrumental techniques are more consistent with each other and the COD than with the BOD. This is because they are all a chemical oxidation whereas the BOD is involved with a biological system. The $\mathrm{TOC/BOD}$ ratio is more uniform because the TOC measures the carbon which the bacteria consume when they use the oxygen. The TOD will give the highest demand value because it measures all the materials which consume oxygen, and the $\mathrm{CO}_2\mathrm{D}$ will generally be very close to the COD .

Table VIII

COMPARISON OF COD AND CARBON (Ref. 9)

	COD	Carbon	COD/Carbon	
Compound	(mg/lit)	(mg/lit)	Calcd	Found
Acetone	61.1	25.0	3.56	2.41
Benzoic acid	73.7	25.0	2.86	2.95
Ethanol	83.8	25.0	4.00	3.35
EDTA	38.6	23.5	2.26	1.64
Glycine	35.4	25.0	2.00	1.42
Sodium lauryl sulfate	43.8	25.0	3.88	1.75
Hydracrylonitrile	68.1	25.0	2.89	2.72
Sodium Oleate	30.8	25.0	3.77	1.59
Pheno1	74.1	25.0	3.11	2.96
Pyridine (HC1 salt)	nil	23.9	3.33	ni1
Salicylic acid	70.7	25.0	2.86	2.83
Sucrose	61.1	25.0	2.67	2.44
2,4,5-Trichlorophenol	60.2	25.0	2.45	2.41
Tryptophan	68.8	25.0	2.79	2.75
Urea	2.4	25.0	nil	0.10
Methenol	07.2	25.0	4.00	3.89



Pigure 5. COD, TOC and CO2D Relationships for an Ethyl Cellulose Industrial Waste (Ref. 8)

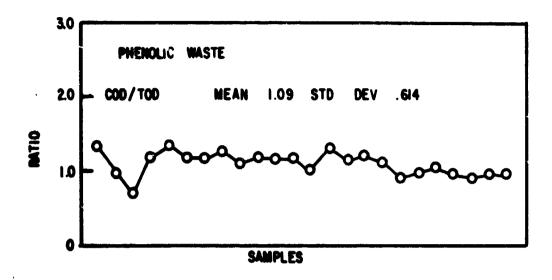


Figure 6. COD/TOD Relationship for a Phenolic Industrial Waste (Ref. 6)

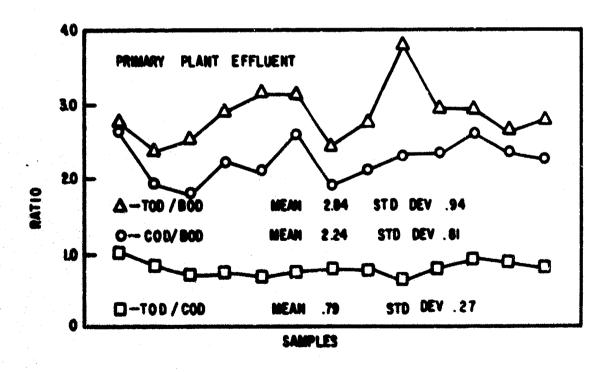


Figure 7. BOD, COD, and TOD Relationships for the Effluent of a Primary Sewage Treatment Plant (Ref. 6)

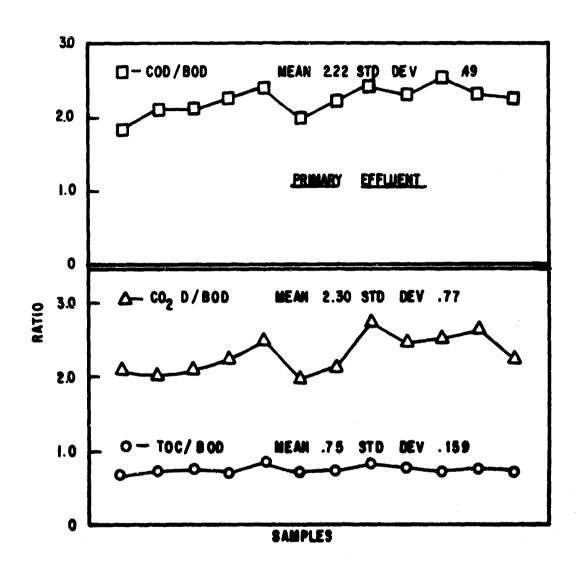


Figure 8. BOD, COD, and TOC Relationships for the Effluent of a Primary Sewage Treatment Plant (Ref. 8)

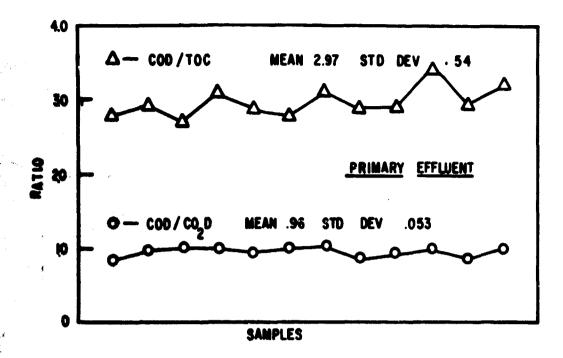


Figure 9. COD, CO₂D, and TOC Relationships for the Effluent of a Primary Sewage Treatment Plant (Ref. 8)

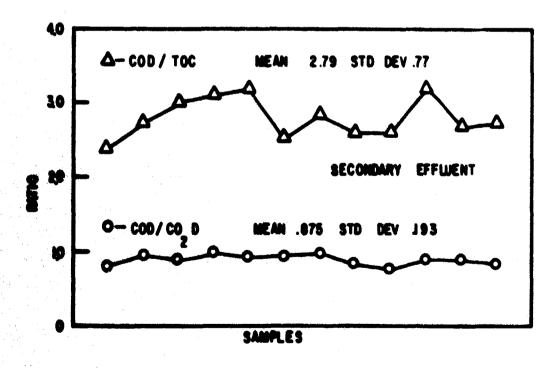


Figure 10. COD, CO₂D, and TOC Relationships for the Effluent of a Secondary Sewage Treatment Plant (Ref. 8)

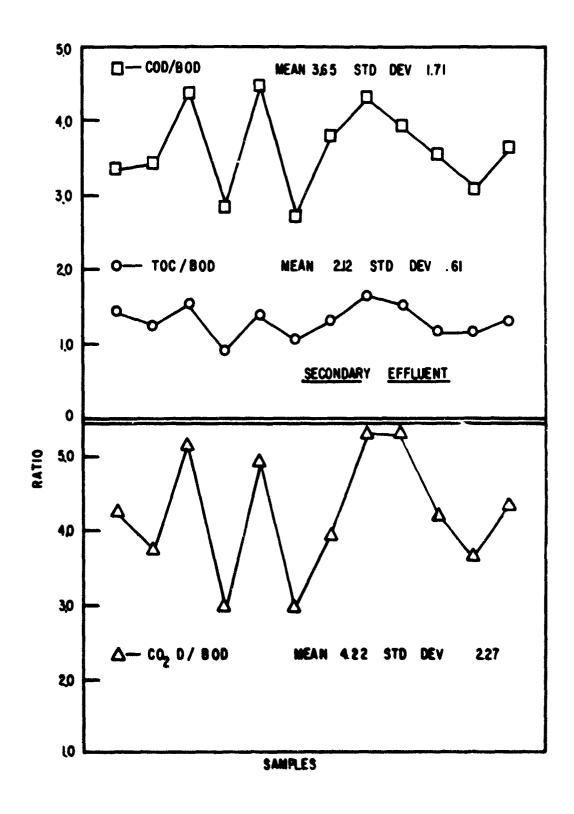


Figure 11. BOD, COD, CO₂D, and TOC Relationships for the Effluent of a Secondary Sewage Treatment Plant (Ref. 8)

SECTION VI

CONCLUSIONS

The use of TOC, TOD, CO₂D analyses will be a definite asset to the water pollution field. The availability of these techniques will replace in many instances the tedious BOD and COD tests with a quicker, more reproducible technique, and will enable the treatment plant operators to make necessary ajustments in plant operation. In addition, it will give the pollution control agencies a more accurate test for determining stream pollution.

The use of these instruments should not be limited to the field analysis of waste water. They can be used very effectively in the research laboratory. Examples of this are monitoring oxidation reactions, evaluating ion exchange or activated carbon capacities, measuring solvent extraction of organics, and determining bacterial culture densities. The applications of Total Organic Carbon (TOC), Total Oxygen Demand (TOD), and Carbon Dioxide Demand (CO,D) are expanding and will continue to gain further acceptance as more data becomes available and as persons in the field become aware of advantages of their use.

REFERENCES

- 1. Standard Methods for the Examination of Water and Waste Water, 11th Edition, American Public Health Association, 1960.
- 2. Ballinger, D. G., and Liska, R. J., "Reliability and Precision of BOD and COD Determinations," Journal Water Pollution Control Federation, May 1962.
- 3. Busch, A. W., "Carbon Analysis as a Concept and Procedure in Water Pollution Technology," <u>Beckman Analyzer</u>, <u>8</u> (1) February 1967.
- 4. Weber, W. J., and Morris, J. C., "Determination of Carbon in Waste Waters by High Temperative Wet Oxidation," <u>Journal Water Pollution Control Federation</u>, May 1964.
- 5. Van Hal', E. E., et al., "Rapid Combustion Method for Determination of Organic Substances in Aqueous Solutions," Anal. Chem. 35, 1963.
- 6. Goldstein, A. L., Katz, W. E., Meller, F. H., Murdock, D. M., "Total Oxygen Demand A New Automatic Instrumental Method for Measuring Pollution and Loading on Oxidation Processes," paper presented 12 September 1968, American Chemical Society Meeting, Atlantic City, New Jersey.
- 7. Van Hall, C. E., and Stenger, V. A., "An Instrumental Method for Rapid Determination of Carbonate and Total Carbon in Solutions," <u>Anal. Chem.</u> 39, 1967.
- 8. Stenger, V. A., Van Hall, C. E., "Rapid Method for Determination of Chemical Oxygen Demand," Anal. Chem. 29, 1967.
- 9. Schaffer, R. B., et al., "Application of a Carbon Analyzer in Waste Treatment,"

 <u>Journal Water Pollution Control Federation</u>, November 1965.
- 10. Stenger, V. A., and Van Hall, C. E., "Applications of a Rapid Technique for COD Determinations," paper presented 24-27 October 1966, Instrumentation Society of American Conference, New York, New York.

BIBLIOGRAPHY

- Gropper, F. R., Heineky, P. M., Westwell, A., "The Determination of Total Organic Matter (Carbon Content) in Aqueous Media," Analyst, 92, 1967.
- Dobbs, R. A., Wise, R. H., Dean, R. B., "Measurement of Organic Carbon in Water Using the Hydrogen Flame Ionization Detector," Anal. Chem. 39 (11), 1967.
- Ford, D. L., "Total Organic Carbon as a Wastewater Parameter," Public Works 89, 1968.
- Kiselbach, R., "Continuous Recording of Concentration of Organic Matter is Waste Water," Anal. Chem. 26, 1954.
- Stenger, V. A., Van Hall, C. E., "Analysis of Municipal and Chemical Wastewaters by an Instrumental Method for COD Determination," <u>Journal Water Pollution</u> <u>Control Federation</u>, 40 (10), 1968.
- Porter, K., and Volman, D. H., "Flame Ionization Detection of Carbon Monoxide for Gas Chromatographic Analysis," Anal. Chem. 34, 1962.
- Van Hall, C. E., et al., "Elimination of carbonates from Aqueous Solutions Prior to Organic Carbon Determination," Anal. Chem. 37, 1965.

UNCLASSIFIED

Security Classification					
DOCUMENT CONT	ROL DATA - R	& D			
(Security classification of title, body of abatmet and indexing	annotation must be e		عدود والمساورين فيتعلق النبكات ويجرب		
RIGINATING ACTIVITY (Corporate author)		20. REPORT SECURITY CLASSIFICATION			
Air Force Weapons Laboratory (WLDC)	7	Inc.	lassified		
Kirtland Air Force Base, New Mexico 8711	. /	ZD. GROUP			
S. REPORT TITLE		<u> </u>			
RAPID INSTRUMENTATION METHODS FOR WATER P	OLLUTION ANA	LYSIS			
4. DESCRIPTIVE NOTES (Type of report and inclusive dates)	······································				
1 December 1968 to 1 February 1969					
5. AUTHOR(8) (First name, middle initial, last name)					
Michael G. MacNaughton, Captain, USAF					
S. REPORT DATE	74. TOTAL NO. O	FPAGES	75. NO. OF REFS		
March 1969	36		10		
SE. CONTRACT OR GRANT NO.	M. ORIGINATOR'S	REPORT NUM	BER(3)		
b. PROJECT NO. 5713	AFWI-TR-6	TR-69-22			
c. Task 25	eb. OTHER REPOR	RT NO(8) (527 ol	ther numbers that may be eastgreed		
d.					
transmittal to foreign governments or for approval of AFWL (WLDC), Kirtland AFB, NM of the technology discussed in the report	eign nationa ex 37117.	is may be Distributi	made only with prior on is limited because		
(Distribution Limitation Stateme	mining the p		•		
treatment plant or a stream. These are T	otal Organic	Carbon (T	OC), Total Grygen		
Demand (TOD), and the Carbon Dioxide Dema	nd (CO ₂ D).	All of the	se can be used to		
replace or supplement the conventional Bi	ochemical Ox	ygen Deman	d (BOD) and Chemical		
Oxygen Demand (COD) procedures. \ The use		-			
(·		
reproducible results and will reduce the	analysis tim	e from hou	rs (COD) and days		
(BOD) to an almost instantaneous readout.	Graphs whi	ch show th	e relationship		
between the three techniques and the conv	entional COD	and BOD t	ests are included		
for industrial and domestic wastes.					
`\					
`					

DD . FORM .. 1473

UNCLASSIFIED
Security Classification

Unclassified

Security Classification LINK A LINK B LINK							
KEY WORDS	HOLE	HOLE WY		LINK B		LINK C	
	MOLE	- · ·	HOI.E	- W 1	HOLF		
Water pollution							
Orygen demand							
Biochemical oxygen demand							
Total organic carbon	ł						
Total oxygen demand]						
Chemical oxygen demand							
Pollution instrumentation							
Soliditou Tuerramentation							
	Ì						
	ļ					1	
	1					,	
						1	
		i	İ			ļ	
			<u> </u>		Ì '	1	
		}	[} .	{	
	ł]	1	
]]	1	
	ļ	1	[<u> </u>			
	1				[Į	
]	ļ			[
	1]	}		\	1	
		ĺ	Į		! .	i	
	}	1			.	1	
		1	,				
		j	İ				
]]	•]	
	1	1	}				
	ļ		1		Ì		
		i				İ	
	1	1	\		1		
	\ \	İ	Į		l		
					1		
	}	[į.		}	}	
		l			[
	Ţ			İ			
	}	1	j		1	1	
	l	Į	Į		l	[
	1	ļ	l		1	1	
	}	1	1		1		
	1		1		1]	
	j	1]]	1]	
	`	1	1	1		1	
				}			
	Ì	1	i)		ì	
	1	1	}			ļ	
	1	1	1	}	1	1	
	1]				1	
	1	1			}	1	
	1		1	[1		
		1		ļ			
		j	1	1	1	1	
	ļ	l	[Į.	Į.		
			ł	İ		1	
	1]]	}		
	1]]	1]	Ì	
	i i	l	l	ŧ	l	Į.	

Unclassified
Security Classification